

Fractional power-law susceptibility and specific heat in low temperature insulating state of o-TaS₃

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Abstract. – Measurements of the magnetic susceptibility and its anisotropy in the quasi-one-dimensional system o-TaS₃ in its low-T charge density wave (CDW) ground state are reported. Both sets of data reveal below 40 K an extra paramagnetic contribution obeying a power-law temperature dependence $\chi(T)=AT^{-0.7}$. The fact that the extra term measured previously in specific heat in zero field, ascribed to low-energy CDW excitations, also follows a power law $C_{LEE}(0,T)=CT^{0.3}$, strongly revives the case of random exchange spin chains. Introduced impurities (0.5% Nb) only increase the amplitude C, but do not change essentially the exponent. Within the two-level system (TLS) model, we estimate from the amplitudes A and C that there is one TLS with a spin $s=1/2$ localized on the chain at the lattice site per cca 900 Ta atoms. We discuss the possibility that it is the charge frozen within a soliton-network below the glass transition $T_g \sim 40$ K determined recently in this system.

The universality of the low-T thermal properties of amorphous materials remains a striking and almost unexplained property. Thus below 1 K, glasses, polymers and amorphous materials exhibit a roughly linear in T extra-phononic contribution to the specific heat C_p , which have commonly been described through the standard model of two-level systems (TLS) intrinsic to structural disorder [1]. However it was demonstrated that randomness can also be revealed in long range order (LRO) ground state. A new class of materials exhibiting low-T universal features of glasses are the quasi one-dimensional conductors in the Peierls state characterized by a periodic lattice distortion accompanied by a charge density wave (CDW) [2]. The model Hamiltonian derived by Fukuyama, Lee and Rice [3] comprises an elastic energy term indicating the ability of the CDW to be stretched or compressed by pinning centers competing with an impurity pinning energy term. The randomness of the CDW ground state is reflected in the existence of many metastable states and hence there is a strong similarity with the X-Y magnet in a random field.

The universality of the disorder property is revealed in an extra-phononic contribution to the specific heat with a smooth variation $C_p \propto T^\nu$ in various inorganic quasi-1D CDW compounds [4] with $0.2 < \nu < 0.8$. The same kind of contribution has been also found in some organic quasi 1-d conductors exhibiting a SDW or a spin-Peierls ground state, with ν up to

1 [5]. For all these compounds the corresponding LEE excitations demonstrate very peculiar dynamical properties which can be understood only if they are weakly coupled to the phonon bath, underlying a clear difference from the case of conventional glasses [4, 5]. In addition, very specific features are found for the glass transition evidenced in the SDW state [6], as well as in the CDW state [7], demonstrating the essential role of the screening of the CDW deformations by free carriers in the substantial changes in the DW ground state. From this point of view, it is very important to better identify the common microscopic origin of LEEs and more specifically the basic characteristics of the topological disorder, which is naturally expected to be related to the DW superstructure.

The fractional-power dependence of $C_p \sim T^\nu$ is usually described through a singularity in the density of states $n(E) = n_0 \cdot E^{\nu-1}$. The same density of state (DOS) can yield a singular T-dependence of the magnetic susceptibility, $\chi \sim T^{\nu-1}$. The first experimental evidence of this kind of phenomenon has been found in complex salts of tetracyanoquinodimethane (TCNQ) by Bulaevskii et al. [8]. It has been attributed to the strong anisotropy of the electronic structure, which makes the magnetic exchange interaction 1-dimensional (with very weak magnetic interactions between chains) and leads to the singular DOS. In the approach based on the random exchange Heisenberg antiferromagnetic chain (REHAC) model a phenomenological DOS has been used, with parameters n_0 and ν taken from experiment. However, the necessity of a singular distribution of random exchange was disproved since even discrete distribution, as in a chain broken into segments or interrupted strands, yielded universal REHAC features [9]. Altogether, a lot of theoretical work has been devoted to random 1-d magnetic systems (see references in [10] and [11]).

The CDW system which shows the largest LEE contribution to C_p among all DW systems [4, 12] is o-TaS₃. It exhibits a Peierls transition at $T_P=218$ K, below which a CDW develops and turns into a low-T insulating ground state [2]. The exponent $\nu \sim 0.3$ of $C_{LEE} \propto T^\nu$ was low enough for investigation of the possible contribution of the corresponding DOS to the susceptibility as $\chi_{LEE} \propto T^{\nu-1}$. In order to establish the correspondence between the two thermodynamic quantities, and add some more information of the low temperature state, we have performed measurements of the susceptibility and of the susceptibility anisotropy in a wide T-range, from 4 K to 300 K.

Magnetic susceptibility χ was measured by the Faraday method and the susceptibility anisotropy $\Delta\chi$ by a home made highly sensitive quartz torque magnetometer [13]. The sensitivity of $\Delta\chi$ measurement is about 10^{-12} emu/g – for a sample mass of ~ 10 mg. The o-TaS₃ sample was mounted in a strain free manner, without grease or glue, between two thin quartz plates held by a light quartz spring. Note that the sample used for magnetic measurements ($m=7$ mg) was from the same batch as the sample used in the specific heat experiment. It looks like a carpet consisting of a bunch of needles all grown in the same chain direction. The pair of crystal axes perpendicular to chains are most probably oriented at random since no anisotropy was observed in this plane in the whole T-range.

As seen in fig. 1, both measurements, χ (fig. 1a) and surprisingly $\Delta\chi$ (fig. 1b) reveal a relatively large low-T upturn. Judging from the similar T-dependence of χ and $\Delta\chi$ and from the fact that the absolute value of $\Delta\chi$ is up to about 10% of χ , $\Delta\chi$ seems to show up via electron spin g-factor anisotropy. Inset in fig. 1a displays the correlation between χ and $\Delta\chi$, showing their proportionality in the whole T-range, which brings the verification that the assumed source of the anisotropy originates from the g-factor anisotropy. Furthermore, the absence of any break in the slope proves that the low-T upturn is caused by the same spin carrying magnetic species; those also giving the intrinsic paramagnetism dominant above 40 K. This high temperature behaviour, unexpected for CDW formation, will be discussed elsewhere.

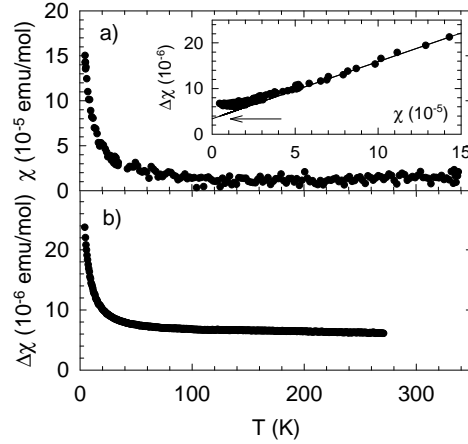


Fig. 1 – χ (a) and $\Delta\chi$ (b) versus temperature for o-TaS₃ both show low-T upturn. The inset in (a) demonstrates the linear correlation between both sets of data and the possible estimation of the correction value indicated by the arrow.

It should be noticed that the small intercept on $\Delta\chi$ and/or χ axes for $T \rightarrow 0$ shows that either the corrections made to the measured χ (tabulated Pascal constants) may not be correct, or some T-independent contribution to $\Delta\chi$ is present. The importance of the proper correction is clearly demonstrated in fig. 2, which displays χ and $\Delta\chi$ versus temperature in a log-log plot. It shows that both measurements can fit the power law $A \cdot T^{\nu-1}$, but some corrections should be made to achieve the same exponent ⁽¹⁾. The appropriate correcting values should be within the limits of a given intercept on χ and/or $\Delta\chi$ axes displayed in the inset of fig. 1a. One way is to subtract only the small intercept on the $\Delta\chi$ axis from the measured anisotropy, i.e. $-3.4 \cdot 10^{-6}$ emu/mole marked by the arrow, what results both, in the linear correlation and the exponent $\nu - 1 = -0.694$ equal to that one of χ (-0.696).

There are a few important conclusions which can be drawn from these results. First, the fact that $\Delta\chi$ in this weak paramagnetic material also exhibits low temperature upturn, indicates the presence of the paramagnetic “impurities” *located on the lattice sites*. Otherwise, as in most cases when paramagnetic impurities are at random, the contributions to the measured $\Delta\chi$ caused by the g-factor anisotropy in average would cancel out. Second, $\Delta\chi$ measurements, being more sensitive, enable us to define more precisely the exponent $\alpha = \nu - 1$ and also the T-range of the power law fit which reflects the range of the exchange interaction J_L between localized magnetic species. In the absence of downwards deviation of the anisotropy from the power-law up to 30 K, we can estimate the lower limit of the corresponding magnetic interaction at low-T: $J_L \sim 30\text{-}40$ K [13]. Unfortunately, without the exact ESR g-factor values $\Delta\chi$ measurements cannot be used for the estimation of the number of paramagnetic “impurities” contained in the power law prefactor A. Third point is the estimation of the concentration of the paramagnetic “impurities”. There are few approaches and regardless the applied model [10,13], the variation is within 50%. At this place, before entering a discussion about the origin of these magnetic species, we choose the extreme case – “impurities” being

⁽¹⁾In the course of the intrinsic susceptibility evaluation where relatively large low temperature upturn has to be subtracted from the small susceptibility values, the choice of the subtracting procedure becomes delicate. We find that between the three possibilities of the low temperature upturn description: the Curie law $C \cdot T^{-1}$, the Curie-Weiss law and the $A \cdot T^{\nu-1}$ power law, the power law appears to be the most appropriate one.

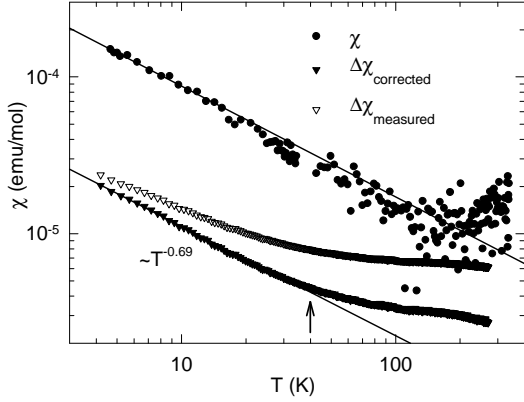


Fig. 2

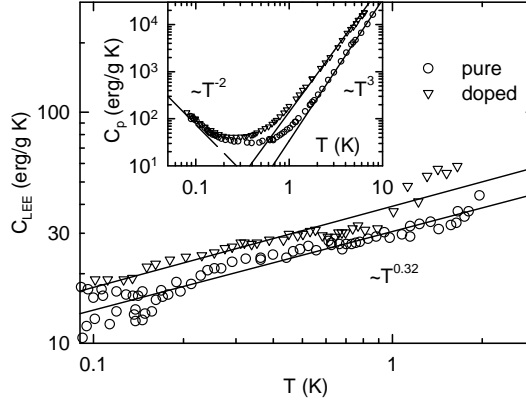


Fig. 3

Fig. 2 – Log-log plots of χ and $\Delta\chi$ versus T exhibit the same power-law dependence after the correction (explained in the text) is done. The arrow points to $J \sim T_g \sim 40$ K [8].

Fig. 3 – Heat capacity of pure and Nb-doped (0.5% nominal) o-TaS₃ between 0.1 K and 7 K, analysed following eq. (1). In the inset is shown the total C_p . Main figure shows power law contributions of the LEEs obtained after subtraction of T^{-2} and C_l contributions.

free spins. By assuming a Curie law with a constant $C_c = A = 4.310^{-4} \text{K}^{-0.3} \text{ emu/mol}$ from $\chi(T < 4 \text{ K})$ data we obtain the spin concentration $c = 1.15 \cdot 10^{-3} \text{ mol}^{-1}$. Within the purely 1-d REHAC model, it yields linear concentration of $3.3 \cdot 10^4 \text{ cm}^{-1}$ per chain. It means that the spins of $s=1/2$ break the Ta-chain into segments of cca 900 Ta atoms.

The heat capacity was measured in a dilution refrigerator by means of a conventional heat-pulse transient technique [5,12]. When the regular phonon contribution, generally in T^3 , and a "hyperfine" contribution in T^{-2} are subtracted, an excess specific heat remains below 1K the T -dependence of which shows a power law $C \cdot T^\nu$ [12]. The total heat capacity for pure and Nb-doped o-TaS₃ samples is reported in inset of fig. 3. Starting from a common lowest- T hyperfine contribution $C_h \cdot T^{-2}$, the heat capacity of the doped sample shows a larger value in the upper T -range, in particular above $T \sim 2$ K where C_p is dominated by the lattice contribution C_l . We believe that this enhancement is due to the strong defective effect (point-defects) induced by the atomic substitution of the Ta atoms by lighter isoelectronic Nb atoms, which in particular results in variation of $C_l(T)$ slower than cubic.

We analysed C_p in the investigated T -range as the sum of three contributions. The two first are originating from C_{LEE} - decomposed into the hyperfine term $C_h \cdot T^{-2}$ and the power-law T^ν [14] and the third one is of vibrational origin:

$$C_p = C_h \cdot T^{-2} + C \cdot T^\nu + C_l \quad (1)$$

The parameters of fits for both curves are given in table I.

The main result of this analysis is the increase of the amplitude C of the power law contribution in the doped sample by cca 30%, whereas the exponent is preserved, as demonstrated in fig. 3. It is known from our previous work that the exponent ν in the power law contribution is a very specific characteristics of the investigated CDW system [4], but it does not change for different sample batches or even for doping [15], hinting to an intrinsic property of each ground state. The same has been also found in REHAC systems with similar consequences

TABLE I – *Parameters of the fits of C_p experimental data to the eq. (1) for pure and 0.5% Nb-doped TaS_3 .*

o-TaS_3	C_h (erg K/g)	C_l (erg/g K)	C (erg/g K ^{1.32})	ν
pure	0.75	34 T ³	30	0.32 ± 0.02
Nb doped	0.75	140 T ^{2.65}	40	0.32 ± 0.02

on doping [10] (note that we do not discuss the irradiation effect).

As we noticed, this power law dependence of the specific heat and magnetic susceptibility can be treated through the phenomenological DOS, $n(E)=n_0E^{\nu-1}$, with two adjustable parameters. The calculation of the DOS depends slightly on the type of excitations and the difference appears only in the amplitude n_0 . In order to calculate the DOS of the LEE, we start with the hypothesis generally admitted [16] that CDW metastable states correspond to TLS-type excitations rather than harmonic oscillators. Indeed the possibility of anharmonicity, in particular if the LEE are related to the pinning centers, is better described by the general anharmonic character of the double well potential of the TLS [17, 18] in comparison to the single well harmonic potential. Within this frame, we have calculated the number of TLS

$$n = \int n(E)dE = 1.05 \cdot 10^{34} \int_{0.1 \text{ K}}^{40 \text{ K}} E^{-0.68} dE \quad (2)$$

$n(E)$ expressed in units states/erg cm³, over the energy range 0.1 K to 40 K (note that $E=2.5 \text{ k}_B T$ is the dominant energy splitting contributing to C_p measured at T). The upper limit corresponds (for being consistent with the susceptibility) to the low-T magnetic interaction $J_L(=k_B T)$ indicated in fig. 2. Therefrom we can get an estimation of the concentration of the LEE by comparison to $N=6.021 \cdot 10^{23}$ structural units defined by the chemical formula (with $M=277 \text{ g/mol}$), being 1030 ppm⁽²⁾, very close to the value 1150 ppm obtained from the susceptibility using Curie law! So, each TLS excitation is related to one spin $s=1/2$.

What is the real nature of these excitations? Overall features resemble the widely investigated REHAC phenomenon with spin $s=1/2$ [8, 9, 10] demonstrating “standard” fractional-power law thermodynamical properties found in a wide family of organic charge transfer salts. Unfortunately, the nature of the elementary excitations of REHAC has not yet been elucidated, nor is it known what is their degree of localization and how it is related to the distribution of magnetic interaction [10]. In the following we intend to propose the real microscopic picture of these excitations in o-TaS₃, to the best of our knowledge the first inorganic system demonstrating REHAC properties.

We notice first that o-TaS₃ exhibits very close exponents ν and α , and even the same effects on doping as REHAC, but the great difference appears in the amplitudes of the investigated thermodynamical properties and the corresponding number of paramagnetic “impurities”, as we provisionally named these low-energy elementary excitations. The REHAC contribution to the specific heat of mostly investigated Q(TCNQ)₂ [10] is $C_{spin}=23.6 \text{ T}^{0.18} \text{ mJ/molK}$, 30 times larger at 1 K than in o-TaS₃ (with comparable lattice contribution)! Similarly, the estimated number of spins responsible for the low-T magnetic properties was found to be in the range from 3% to 10% [10, 9], more than 30 times larger than in o-TaS₃! We might say that o-TaS₃ is an inorganic REHAC system in a highly “diluted” limit of paramagnetic “impurities”. Those

⁽²⁾For comparison, note that the integration up to $E=30 \text{ K}$ yields a concentration of 920 ppm.

impurities are spins of $s=1/2$ sparsely placed on the lattice sites cca every 900 Å distances or 3000 Å, interacting with $J_L \sim 30\text{-}40$ K, which give rise to the typical REHAC behaviour.

The basic characteristics of REHAC - the disorder and localization - are inherent to the CDW ground state; so it is not surprising that both length scale and energy scale obtained from the REHAC behaviour are deeply related to the CDW ground state of o-TaS₃. In fact for being more explicit, we believe that it is one additional manifestation of the change within the CDW ground state occurring at low-T. We have recently demonstrated that the low temperature ground state of o-TaS₃ is reached through the glass transition on the level of the CDW superstructure [7]. We have related it to the freezing of dynamics of CDW phase domains due to the Coulomb hardening in the absence of free carrier screening. The estimate of the critical free carrier density $n_e(T_g)$ which leads to freezing, to be about 10^{15} e/cm³, is consistent with charge frozen at T_g as obtained from thermally stimulated discharge [19]. The corresponding volume of 10^{-15} cm³ per free carrier is close to the estimates of the phase coherence volume, and it might be at the origin of the twinkling domains seen in TEM [20] which have just the right size ($\sim 4000 \times 300 \times 300$ Å³ $\approx 4 \cdot 10^{-16}$ cm³).

Remaining degrees of freedom below T_g have been associated with topological defects of phase such as solitons, domain walls or dislocation loops. REHAC behaviour, which is essentially related to 1-dimensionality, can help in further understanding of LEE at low temperatures. Recent analysis of the properties of CDW in the low-T insulating phase [21] has shown that soliton-like defects on single chain, which perturb very weakly the phase on adjacent chains, can exist due to nonlinear screening. In typical conditions easily met in insulating CDW systems such solitons would change local value of electrochemical potential allowing creation of strongly 1-d metallic islands. Slight overlap of these islands can explain, for instance, enhanced conductivity observed (only) in the chain direction [22]. More important for us, these metallic islands can give localized unpaired spins leading to the REHAC behaviour due to the inherent strong anisotropy. We should add that this is not the single possible explanation, as there exist more exotic species of solitons that can have spin *per se* [23].

There should exist some fine tuning mechanism coming from the interaction with underlying lattice responsible for so specific positions of the REHAC excitations. A strong influence of the CDW on the lattice has been demonstrated in o-TaS₃ [24]. The glass transition itself leaves some fingerprints on the phonon dynamics [25]. STM studies showed, that in addition to very complicated structure of o-TaS₃, there are two CDW maxima per unit cell along the b_0 direction which are strongly correlated, so that they respond with a single Peierls transition. As there is no chain staggering, the CDW maxima are adjacent to each other and the Coulomb repulsion encourages the uniform distribution of the CDW within the unit cell (i.e. they are not localized on any particular chains) [26]. It is very probable that the origin of the preferred position of the REHAC elementary excitation are the CDW dynamical defects, as sudden sliding of CDW for one lattice spacing in the chain direction has been observed even at room T [26]. In this very delicate entanglement of the lattice and CDW(s), it might be that the lattice tries to stagger the chains in order to reduce the Coulomb repulsion. On approaching the glass transition the Coulomb hardening of the CDW forces the CDW wave vector to fit the commensurate value $q_{2k_F}=1/4$ c_0 . Hence, the solitons, being the defects of the CDW superstructure, tend to have preferential positions. Finally, also the structural defects might be dragged by the CDW and frozen together on the edges of the Lee-Rice domains, consistent with our previous discussion.

In conclusion, we would like to stress the importance of the detailed specification of low-T CDW excitations yielding the characteristic REHAC behaviour, equally from the experimental point of view, as well as theoretical one. Charge-spin mixing properties are essentially important as it is known that in CDW the soliton generates a localized region of a SDW and

a net spin (and vice versa) [23]. The problem of various kinds of solitons, self trapping and/or self doping seems to be a central point. Some further comparison with "classical" REHAC behaviour, especially concerning the dynamical manifestations, might give some answers on the relevance of the lengths of correlations (LRO/SRO) in the corresponding ground states.

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